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Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

99204566.6

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

I.L.C. HATTEN-HECKMAN

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Blatt 2 der B scheinigung
Sheet 2 of the certificate
Page 2 de l'attestation

Anmeldung Nr.:
Application no.: **99204566.6**
Demande n°:

Anmeldetag:
Date of filing: **28/12/99**
Date de dépôt:

Anmelder:
Applicant(s):
Demandeur(s):
Montell Technology Company bv
2132 MS Hoofddorp
NETHERLANDS

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:
Process for the preparation of ethylene polymers

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat: State: Pays:	Tag: Date: Date:	Aktenzeichen: File no. Numéro de dépôt:
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Internationale Patentklassifikation:
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/

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Contracting states designated at date of filing: AT/B/E/CH/C/Y/DE/DK/ES/F/I/FR/GB/GR/IE/IT/LI/LU/MC/NL/PL/PT/SE/TR
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28-12-1999

EP99204566.6

SPEC

TC 5421

TITLE:

PROCESS FOR THE PREPARATION OF ETHYLENE POLYMERS

The present invention relates to a polymerization process for the preparation of polymers of ethylene in the presence of a metallocene catalyst. The invention also relates to a process for preparing the corresponding ligands useful as intermediates in the synthesis of said metallocene compounds.

Metallocene compounds having two bridged cyclopentadienyl groups are known as catalyst components for the homo- and copolymerization reaction of ethylene.

For example, EP-A-0 399 348 describe the polymerization of ethylene in the presence of indenyl based metallocenes. Although the polyethylene obtained has industrially acceptable molecular weight, the metallocene used in the polymerization process has low polymerization activity.

More recently, heterocyclic metallocene compounds used in the polymerization of alpha-olefins have been described.

In International application WO 98/22486 it is described a class of metallocenes containing a cyclopentadienyl radical directly coordinating the central metal atom, to which are fused one or more rings containing at least one heteroatom. These metallocenes, in combination with a suitable cocatalyst, are used in the polymerization of olefins such as ethylene. However, the molecular weights that can be obtained at polymerization temperatures of industrial interest are still too low for many applications and the activity of these catalyst systems, when used in the polymerization of ethylene, is not satisfactory.

It would be desirable to identify metallocenes which, when used in catalysts for the polymerization of ethylene, have high activity, such that the amount of the catalyst remaining in the polymer is minimized, and are capable of yielding polymers endowed with high molecular weights.

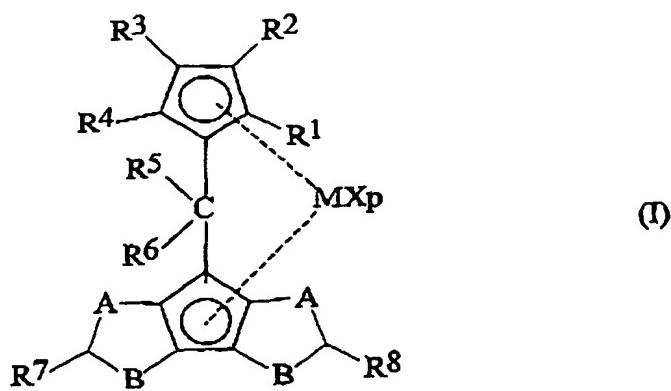
It has been unexpectedly found that it is possible to prepare ethylene polymers having high molecular weights with high yields, operating at temperatures of industrial interest, by carrying out the polymerization reaction of ethylene in the presence of a catalyst based on a class of heteroatom containing metallocene compounds.

Thus, according to a first aspect of the present invention, it is provided a process for the preparation of polymers of ethylene comprising the polymerization reaction of ethylene in the presence of a catalyst comprising the product obtainable by contacting:

(A) metallocene compound of the formula (I):

(TC 5421.EP)

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wherein

A and B are selected from S, O and CR⁹, R⁹ being selected from hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, C₇-C₂₀-arylalkyl radical, optionally containing a heteroatom, either A or B being different from CR⁹, and wherein the rings containing A and B have a double bond in the allowed position;

R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, and R⁹, same or different, are selected from hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, C₇-C₂₀-arylalkyl radical, optionally containing a heteroatom, and two adjacent R¹ and R² and/or R³ and R⁴ and/or R⁵ and R⁶ can form a ring comprising 4 to 8 atoms, which can bear substituents;

with the proviso that at least one of R¹, R², R³, R⁴, R⁷ and R⁸ is not hydrogen;

M is an atom of a transition metal selected from those belonging to group 3, 4, 5, 6 or to the lanthanide or actinide groups in the Periodic Table of the Elements (new IUPAC version),

X, same or different, is a halogen atom, a R¹⁰, OR¹⁰, OSO₂CF₃, OCOR¹⁰, SR¹⁰, NR¹⁰₂ or PR¹⁰₂ group, wherein the substituents R¹⁰ are selected from hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, C₇-C₂₀-arylalkyl radical, optionally containing a heteroatom;

p is an integer of from 0 to 3, being equal to the oxidation state of the metal M minus 2

and

(B) an alumoxane and/or a compound capable of forming an alkyl metallocene cation.

The transition metal M is preferably selected from titanium, zirconium and hafnium. Most preferably, the transition metal M is zirconium.

The X substituents are preferably chlorine atoms or methyl groups. Most preferably X are chlorine atoms.

Preferably A and B are selected from sulfur and a CH group, either A or B being different from CH, R¹, R³ and R⁴ are hydrogen, R⁵ and R⁶ are C₁-C₂₀-alkyl groups, such as methyl, and R⁷ is equal to R⁸.

Most preferably, R¹ are hydrogen or C₁-C₂₀-alkyl groups, such as methyl or ter-butyl, and R⁷ and R⁸ are hydrogen or methyl groups.

Non-limiting examples of metallocene compounds suitable for use in the process of the invention are:

methylene(3-trimethylsilyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;

methylene(cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;

methylene(3-trimethylsilyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;

methylene(3-methyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;

methylene(3-methyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'] dioxazole)zirconium dichloride and dimethyl;

methylene(cyclopentadienyl)-7-(2,5-dimethylphosphinocyclopentadienyl-[1,2-b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;

methylene(cyclopentadienyl)-7-(2,5-dimethylphosphinocyclopentadienyl-[1,2-b:4,3-b'] dioxazole)zirconium dichloride and dimethyl;

methylene(cyclopentadienyl)-7-(2,5-diphenylphosphinocyclopentadienyl-[1,2-b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;

methylene(cyclopentadienyl)-7-(2,5-dimethoxyphosphinocyclopentadienyl-[1,2-b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;

methylene(cyclopentadienyl)-7-(2,5-dimethoxyborylcyclopentadienyl-[1,2-b:4,3-b'] dithiophene)zirconium dichloride and dimethyl;

methylene(cyclopentadienyl)-7-(2,5-dimethoxycyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(3-methoxycyclopentadienyl)-7-(2,5-dimethoxycyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(cyclopentadienyl)-7-(2,5-dithiocyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(3-methyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(3-ethyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(3-isopropyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(3-tert-butyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(3-phenyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(2,3-dimethyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(2,3-diethyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(2,3-diisopropyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(2,3-ditert-butyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,5-trimethyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,5-triethyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,5-triisopropyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,5-tritert-butyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])

dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,4,5-tetramethyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,4,5-tetraethyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,4,5-tetraisopropyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
isopropylidene(3-trimethylsilyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
isopropylidene(cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
isopropylidene(cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b'])
dioxazole)zirconium dichloride and dimethyl;
isopropylidene(3-trimethylsilyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
isopropylidene(cyclopentadienyl)-7-(2,5-dimethylphosphinocyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
isopropylidene(cyclopentadienyl)-7-(2,5-dimethylphosphinocyclopentadienyl-[1,2-b:4,3-b'])
dioxazole)zirconium dichloride and dimethyl;
isopropylidene(cyclopentadienyl)-7-(2,5-diphenylphosphinocyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
isopropylidene(cyclopentadienyl)-7-(2,5-dimethoxyphosphinocyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
isopropylidene(cyclopentadienyl)-7-(2,5-dimethoxyborylcyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
isopropylidene(cyclopentadienyl)-7-(2,5-dimethoxycyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
isopropylidene(3-methoxycyclopentadienyl)-7-(2,5-dimethoxycyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
isopropylidene(cyclopentadienyl)-7-(2,5-dithiocyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-methyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
isopropylidene(3-ethyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
isopropylidene(3-isopropyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
isopropylidene(3-tert-butyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'])
dithiophene)zirconium dichloride and dimethyl;
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dithiophene)zirconium dichloride and dimethyl;
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dithiophene)zirconium dichloride and dimethyl;
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dithiophene)zirconium dichloride and dimethyl;
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dithiophene)zirconium dichloride and dimethyl;
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methylene(3-ethyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride and dimethyl;
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methylene(3-tert-butyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride and dimethyl;
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b:4,3-b']-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3-ditert-butyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3,5-trimethyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride and dimethyl;
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isopropylidene(2,3,4,5-tetraisopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride and dimethyl;
benzylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride and dimethyl;
benzylidene(3-trimethylsilyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride and dimethyl;
benzylidene(3-methyl-cyclopentadienyl)-7-(2,5-ditrimethylsilyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride and dimethyl;
benzylidene(3-methyl-cyclopentadienyl)-7-(2,5-diethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride and dimethyl;
benzylidene(3-methyl-cyclopentadienyl)-7-(2,5-diethyl-cyclopentadienyl-[1,2-b:4,3-b']-dioxazole)zirconium dichloride and dimethyl;
methylene(3-trimethylsilyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(cyclopentadienyl)-4-(2,5-ditrimethylsilyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

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methylene(cyclopentadienyl)-4-(2,5-ditrimethylsilyl-cyclopentadienyl-[2,1-b:3,4-b']-dioxazole)zirconium dichloride and dimethyl;

methylene(3-trimethylsilyl-cyclopentadienyl)-4-(2,6-ditrimethylsilyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(cyclopentadienyl)-4-(2,6-dimethylphosphinocyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(cyclopentadienyl)-4-(2,6-dimethylphosphinocyclopentadienyl-[2,1-b:3,4-b']-dioxazole)zirconium dichloride and dimethyl;

methylene(cyclopentadienyl)-4-(2,6-diphenylphosphinocyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(cyclopentadienyl)-4-(2,6-dimethoxyphosphinocyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(cyclopentadienyl)-4-(2,6-dimethoxyborylcyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(cyclopentadienyl)-4-(2,6-dimethoxycyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(3-methoxycyclopentadienyl)-4-(2,6-dimethoxycyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(cyclopentadienyl)-4-(2,6-dithiocyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(3-methyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(3-ethyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(3-isopropyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(3-tert-butyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(3-phenyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(2,3-dimethyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-

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dithiophene)zirconium dichloride and dimethyl;
methylene(2,3-diethyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(2,3-diisopropyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(2,3-ditert-butyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,5-trimethyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,5-triethyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,5-triisopropyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,5-tritert-butyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,4,5-tetramethyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,4,5-tetraethyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(2,3,4,5-tetraisopropyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(3-trimethylsilyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(cyclopentadienyl)-4-(2,6-ditrimethylsilyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(3-trimethylsilyl-cyclopentadienyl)-4-(2,6-ditrimethylsilyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(cyclopentadienyl)-4-(2,6-dimethylphosphinocyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(cyclopentadienyl)-4-(2,6-diphenylphosphinocyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(cyclopentadienyl)-4-(2,6-dimethoxyphosphinocyclopentadienyl-[2,1-b:3,4-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(cyclopentadienyl)-4-(2,6-dimethoxyborylcyclopentadienyl-[2,1-b:3,4-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(cyclopentadienyl)-4-(2,6-dimethoxycyclopentadienyl-[2,1-b:3,4-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(cyclopentadienyl)-4-(2,6-dithiocyclopentadienyl-[2,1-b:3,4-b']) dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-methyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-methyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b'])-dioxazole)zirconium dichloride and dimethyl;

isopropylidene(3-ethyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-isopropyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-tert-butyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-phenyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(2,3-dimethyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(2,3-diethyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(2,3-diisopropyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(2,3-ditert-butyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(2,3,5-trimethyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(2,3,5-triethyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b'])-

dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3,5-triisopropyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3,5-tri-tert-butyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3,4,5-tetramethyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3,4,5-tetraethyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3,4,5-tetraisopropyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(3-trimethylsilyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(3-methyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(3-methyl-cyclopentadienyl)-4-(2,6-ditrimethylsilyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(3-ethyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(3-isopropyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(3-isopropyl-cyclopentadienyl)-4-(2,6-ditrimethylsilyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(3-tert-butyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(3-phenyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(2,3-dimethyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
methylene(2,3-diethyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

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methylene(2,3-diisopropyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(2,3-ditert-butyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(2,3,5-trimethyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(2,3,5-triethyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(2,3,5-triisopropyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(2,3,5-tritert-butyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(2,3,4,5-tetramethyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(2,3,4,5-tetraethyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

methylene(2,3,4,5-tetraisopropyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-trimethylsilyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-methyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-methyl-cyclopentadienyl)-4-(2,6-ditrimethylsilyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-ethyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-isopropyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

isopropylidene(3-isopropyl-cyclopentadienyl)-4-(2,6-ditrimethylsilyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;

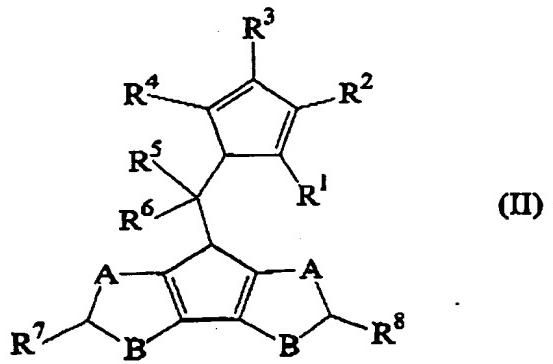
isopropylidene(3-tert-butyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-

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b']-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(3-phenyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3-dimethyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3-dimethyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b'])-dioxazole)zirconium dichloride and dimethyl;
isopropylidene(2,3-dimethyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3-diisopropyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3-ditert-butyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3,5-trimethyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3,5-triethyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3,5-triisopropyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3,5-tricrt-butyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3,4,5-tetramethyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3,4,5-tetraethyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;
isopropylidene(2,3,4,5-tetraisopropyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;
benzylidene(3-trimethylsilyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;
benzylidene(3-methyl-cyclopentadienyl)-4-(2,6-dimethyl-cyclopentadienyl-[2,1-b:3,4-b'])-dithiophene)zirconium dichloride and dimethyl;

benzylidene(3-methyl-cyclopentadienyl)-4-(cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl; isopropylidene(3-trimethylsilyl-cyclopentadienyl)-4-(2-methyl-6-ethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl; isopropylidene(3-methyl-cyclopentadienyl)-4-(2-methyl-6-ethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl; methylene(3-trimethylsilyl-cyclopentadienyl)-4-(2-methyl-6-ethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl; methylene(3-methyl-cyclopentadienyl)-4-(2-methyl-6-ethyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl; isopropylidene(3-trimethylsilyl-cyclopentadienyl)-4-(2-methyl-6-isopropyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl; isopropylidene(3-methyl-cyclopentadienyl)-4-(2-methyl-6-isopropyl-cyclopentadienyl-[2,1-b:3,4-b']-dithiophene)zirconium dichloride and dimethyl.

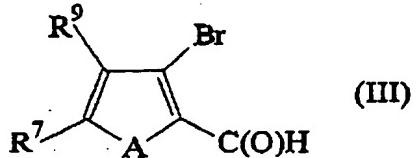
According to a further aspect of the present invention, it is provided a process for the preparation of a ligand of formula (II):



and/or its double bond isomers,

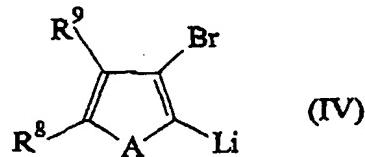
wherein A, B, R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ are defined as above, comprising the following steps:

- a) treating a compound of formula (III):



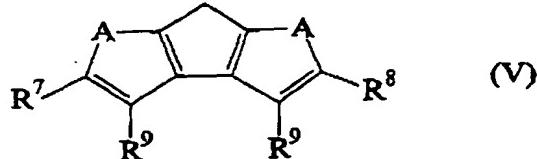
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wherein A is sulfur or oxygen,
with a compound of formula (IV):

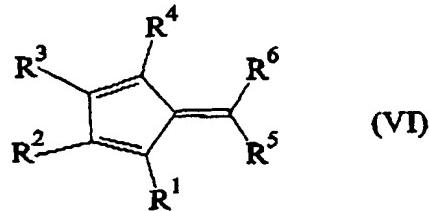


wherein A is sulfur or oxygen,

- b) contacting the thus obtained product with a reducing agent in a molar ratio between said reducing agent and the product obtained under a) of at least 1;
- c) contacting the product obtained under b) with a compound selected from an organic lithium compound, sodium and potassium in a molar ratio between said compound and the product obtained in step b) of equal to or greater than 2;
- d) treating the thus obtained product with an agent selected from the group consisting of copper chloride, iodine and Mg/Pd., in order to obtain a compound of general formula (V):



- e) treating the compound of formula (V) with at least one equivalent of a base;
- f) contacting the thus obtained corresponding anionic compound of formula (V) with a compound of formula (VI):



wherein R¹, R², R³, R⁴, R⁵ and R⁶ are defined as described above, and

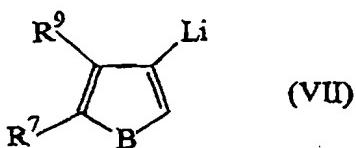
- g) treating the thus obtained product with a protonating agent.

According to a further aspect of the present invention, it is provided a process for the preparation of a ligand of formula (II) as described above, comprising the following steps:

- a) contacting a compound of formula (VII):

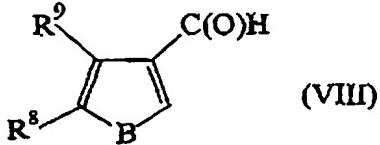
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wherein B is sulfur or oxygen,

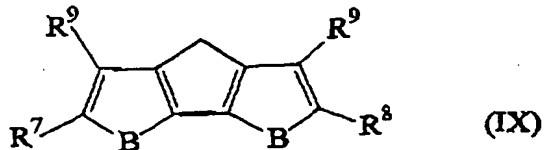
with a compound of formula (VIII):



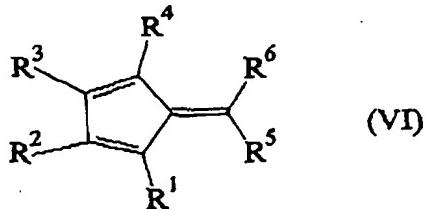
wherein B is sulfur or oxygen,

and subsequently treating with a neutralization agent;

- b) treating the thus obtained product with a reducing agent in a molar ratio between said reducing agent and the compound obtained under a) of at least 1;
- c) contacting the thus obtained product with a mixture of an organic lithium compound and tetramethylethylenediamine (TMEDA) in a molar ratio between said mixture and the product obtained under b) of at least 2;
- d) contacting the thus obtained product with an agent selected from the group consisting of copper chloride, iodine and Mg/Pd., in order to obtain a compound of formula (IX):



- e) treating the compound of formula (IX) with at least one equivalent of a base;
- f) contacting the thus obtained corresponding anionic compound of formula (IX) with a compound of formula (VI):



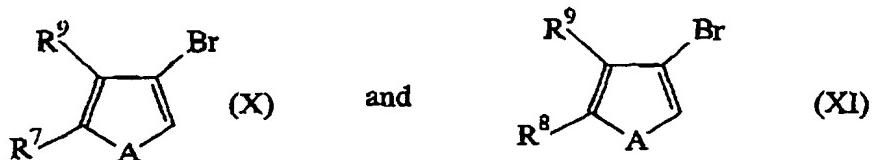
wherein R¹, R², R³, R⁴, R⁵ and R⁶ are defined as described above, and

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g) treating the thus obtained product with a protonating agent.

According to a further aspect of the present invention, it is provided a process for the preparation of a ligand of formula (II) as described above, comprising the following steps:

a) contacting an equimolar mixture of compounds of formulae (X) and (XI):



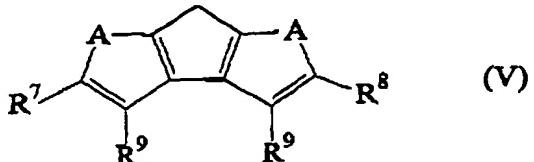
wherein A are sulfur or oxygen,

with a Lewis acid or a mixture of a Lewis acid and a protonic acid;

b) treating the thus obtained product with CH_2O in a molar ratio between said mixture and CH_2O of a range between 10:1 and 1:10;

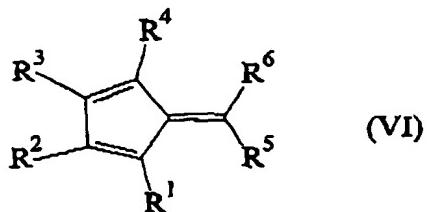
c) contacting the thus obtained product with a compound selected from an organic lithium compound, sodium and potassium;

d) contacting the thus obtained product with an agent selected from the group consisting of copper chloride, iodine and Mg/Pd., in order to obtain a compound of general formula (V)



e) treating the compound of formula (V) with at least one equivalent of a base;

f) contacting the thus obtained corresponding anionic compound of formula (V) with a compound of formula (VI):



wherein R¹, R², R³, R⁴, R⁵ and R⁶ are defined as described above, and

g) treating the thus obtained product with a protonating agent.

When the compounds of formulas (V) and (IX) are treated with at least one equivalent of a

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base said base is preferably selected from hydroxides and hydrides of alkali- and earth-alkali metals, metallic sodium and potassium and organometallic lithium salts. Most preferably, said base is methyllithium or n-butyllithium.

The Lewis acid used in the above processes of the invention is preferably selected from zinc dichloride, cadmium dichloride, mercurium dichloride, tin tetrachloride, trifluoroborane, zirconium tetrachloride, titanium tetrachloride. Most preferably, the Lewis acid is zinc dichloride.

The protonic acid used in the above processes of the invention is preferably selected from sulphuric acid, phosphoric acid, nitric acid and hydrochloric acid. Most preferably hydrochloric acid is used.

The agent used in the above processes of the invention is preferably copper chloride.

Preferably the protonating agent used in the above processes of the invention is a quaternary ammonium salt and most preferably the protonating agent is ammonium chloride.

Preferably the reducing agent is a mixture of $\text{AlCl}_3/\text{LiAlH}_4$.

The organic lithium compound used above is preferably butyllithium.

Compounds of formula (II) can suitable be used as intermediates for the preparation of metallocenes of formula (I).

A further aspect of the present invention is a process for the preparation of a metallocene compound of the formula (I):

comprising the following steps:

- a) contacting a compound of formula (II) as defined above with a base, wherein the molar ratio between said base and the compound of formula (II) is at least 2;
- b) contacting with a compound of formula (XII) MX_p , M and X being defined as mentioned above and p is an integer being equal to the oxidation state of the metal M.

Preferably, the base is butyllithium.

Preferably, MX_p is selected from ZrCl_4 , TiCl_4 , HfCl_4 and the $\text{C}_1\text{-C}_6$ -alkyl analogues thereof.

In the case in which at least one substituent X in the metallocene compound of the formula (I) which is to be prepared is other than a halogen, it is necessary to substitute at least one substituent X in the metallocene obtained by at least one substituent X other than a halogen.

The reaction of substituting substituents X by substituents X other than a halogen is carried out using generally applied methods. For example, if the desired substituents X are alkyl

groups, the metallocenes can be made to react with alkylmagnesium halides (Grignard reagents) or with alkylolithium compounds. General methods for substitution X by substituents other than halogen such as sulfur, phosphorus, oxygen, etc. are described in Chem. Rev. 1994, 94, 1661-1717, and the therein cited references.

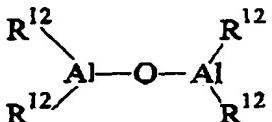
The alumoxane used as component (B) can be obtained by reacting water with an organo-aluminium compound of formula AlR^{11} , or Al_2R^{11} , wherein the R^{11} substituents, same or different from each other, are defined as R^2 . In this reaction the molar ratio of Al/water is comprised between 1:1 and 100:1.

Non-limiting examples of aluminium compounds of the formula AlR^{11} , or Al_2R^{11} , are:

$\text{Al}(\text{Me})_3$, $\text{Al}(\text{Et})_3$, $\text{AlH}(\text{Et})_2$, $\text{Al}(\text{iBu})_3$, $\text{AlH}(\text{iBu})_2$, $\text{Al}(\text{iHex})_3$, $\text{Al}(\text{iOct})_3$, $\text{AlH}(\text{iOct})_2$, $\text{Al}(\text{C}_6\text{H}_5)_3$, $\text{Al}(\text{CH}_2\text{-CH}(\text{Me})\text{CH}(\text{Me}))_2$, $\text{Al}(\text{CH}_2\text{C}_6\text{H}_5)_3$, $\text{Al}(\text{CH}_2\text{CMe}_3)_3$, $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$, $\text{Al}(\text{Me})_2\text{iBu}$, $\text{Al}(\text{Me})_2\text{Et}$, $\text{AlMe}(\text{Et})_2$, $\text{AlMe}(\text{iBu})_2$, $\text{Al}(\text{Me})_2\text{iBu}$, $\text{Al}(\text{Me})_2\text{Cl}$, $\text{Al}(\text{Et})_2\text{Cl}$, AlEtCl_2 and $\text{Al}_2(\text{Et})_3\text{Cl}_3$, wherein Me = methyl, Et = ethyl, iBu = isobutyl, iHex = isohexyl, iOct = 2,4,4-trimethyl-pentyl.

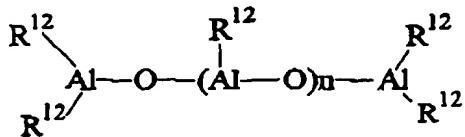
Amongst the above aluminium compounds, trimethylaluminium (TMA), triisobutylaluminium (TIBAL) and tris(2,4,4-trimethyl-pentyl)aluminium (TIOA) are preferred.

The alumoxanes used in the catalyst according to the invention are considered to be linear, branched or cyclic compounds containing at least one group of the type:



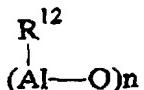
wherein the substituents R^{12} , same or different, are $\text{C}_1\text{-C}_{20}$ -alkyl, $\text{C}_3\text{-C}_{20}$ -cycloalkyl, $\text{C}_2\text{-C}_{20}$ -alkenyl, $\text{C}_6\text{-C}_{20}$ -aryl, $\text{C}_7\text{-C}_{20}$ -alkylaryl or $\text{C}_7\text{-C}_{20}$ -arylalkyl radicals, optionally containing hydrogen atoms, silicon or germanium atoms, or a $-\text{O}-\text{Al}(\text{R}^{12})_2$ group and, if appropriate, some substituents R^{12} can be halogen atoms.

In particular, alumoxanes of the formula:



can be used in the case of linear compounds, wherein n is 0 or an integer of from 1 to 40 and
(TC 5421.EP)

the substituents R¹² are defined as above, or alumoxanes of the formula:



can be used in the case of cyclic compounds, wherein n is an integer of from 2 to 40 and the R¹¹ substituents are defined as above.

The substituents R¹² are preferably ethyl, isobutyl or 2,4,4-trimethyl-pentyl groups.

Examples of alumoxanes suitable for use according to the present invention are methylalumoxane (MAO), isobutylalumoxane (TIBAO) and 2,4,4-trimethyl-pentylalumoxane (TIOAO).

The molar ratio between the aluminium and the metal of the metallocene compound is in general comprised between 10:1 and 20000:1, and preferably between 100:1 and 5000:1.

Non-limiting examples of compounds able to form an alkylmetallocene cation are compounds of the formula Y⁺Z⁻, wherein Y⁺ is a Broensted acid, able to donate a proton and to react irreversibly with a substituent X of the compound of the formula (I), and Z⁻ is a compatible anion which does not coordinate and which is able to stabilize the active catalytic species which results from the reaction of the two compounds and which is sufficiently labile to be displaceable by an olefin substrate. Preferably, the anion Z⁻ consists of one or more boron atoms. More preferably, the anion Z⁻ is an anion of the formula BAr₄⁽⁺⁾, wherein the substituents Ar which can be identical or different are aryl radicals such as phenyl, penta-fluorophenyl or bis(trifluoromethyl)phenyl. Tetrakis-pentafluorophenyl borate is particularly preferred. Moreover, compounds of the formula BAr₃ can conveniently be used. Compounds of this type are described, for example, in the published International patent application WO 92/00333, the content of which is incorporated in the present description.

The catalysts of the present invention can also be used on supports. This is achieved by depositing the metallocene compound (A) or the product of the reaction thereof with the component (B), or the component (B) and then the metallocene compound (A) on supports such as, for example, silica, alumina, magnesium halides, styrene/divinylbenzene copolymers, polyethylene or polypropylene.

A suitable class of supports usable is constituted by porous organic supports functionalized with groups having active hydrogen atoms. Particularly suitable are those in which the organic

support is a partially crosslinked styrene polymer. Supports of this type are described in European application EP-633 272.

Another class of inert supports particularly suitable for use according to the invention is that of the olefin, particularly propylene, porous prepolymers described in International application WO 95/26369.

A further suitable class of inert supports for use according to the invention is that of the porous magnesium halides such as those described in International application WO 95/32995. The solid compound thus obtained, in combination with the further addition of the alkylaluminium compound either as such or prereacted with water if necessary, can be usefully employed in the gas-phase polymerization.

The process for the polymerization of olefins according to the invention can be carried out in the liquid phase in the presence or absence of an inert hydrocarbon solvent, or in the gas phase. The hydrocarbon solvent can either be aromatic such as toluene, or aliphatic such as propane, hexane, heptane, isobutane or cyclohexane.

The polymerization temperature is generally comprised between -100°C and +200°C and, particularly between 10°C and +90°C. The polymerization pressure is generally comprised between 0,5 and 100 bar.

The lower the polymerization temperature, the higher are the resulting molecular weights of the polymers obtained.

The polymerization yields depend on the purity of the metallocene compound of the catalyst. The metallocene compounds obtained by the process of the invention can therefore be used as such or can be subjected to purification treatments.

The components of the catalyst can be brought into contact each other before the polymerization. The pre-contact concentrations are generally between 1 and 10⁻³ mol/l for the metallocene component (A), while they are generally between 10 and 10⁻³ mol/l for the component (B). The pre-contact is generally effected in the presence of a hydrocarbon solvent and, if appropriate, of small quantities of monomer.

By the process according to the present invention ethylene homopolymers are obtainable having high molecular weights. The ethylene polymers of the present invention have intrinsic viscosity (I.V.) values generally higher than 0.5 dl/g, more typically higher than 1.0 dl/g. Particularly in the case of ethylene homopolymers, the intrinsic viscosity can reach values as

high as 5.0 dl/g.

In the copolymers obtainable with the process of the invention, the content by mole of ethylene derived units is generally higher than 40%, and preferably it is comprised between 50% and 99%, and more preferably it is comprised between 80% and 98%.

The molar content of alpha-olefin derived units is preferably comprised between 0% and 60% and, more preferably, between 1% and 50%, and most preferably between 2% and 20%.

Non-limiting examples of alpha-olefins which can be used as alpha-olefins in the process of the invention are propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 4,6-dimethyl-1-heptene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene and allylcyclohexane.

Non-limiting examples of cycloolefins that can be used as comonomers in the process of the invention are cyclopentene, cyclohexene and norbornene.

The copolymers according to the invention can also contain units derived from polyenes. The content of polyene derived units, if any, is preferably comprised between 0% and 30% by mol and, more preferably between 0% and 20%.

The polyenes that can be used as comonomers in the copolymers according to the present invention are comprised in the following classes:

- non-conjugated diolefins able to cyclopolymerize such as, for example, 1,5-hexadiene, 1-6-heptadiene, 2-methyl-1,5-hexadiene;
- dienes capable of giving unsaturated monomeric units, in particular conjugated dienes such as butadiene and isoprene, linear non-conjugated dienes such as trans 1,4-hexadiene, cis 1,4-hexadiene, 6-methyl-1,5-heptadiene, 3,7-dimethyl-1,6-octadiene, 11-methyl-1,10-dodecadiene, and cyclic non-conjugated dienes such as 5-ethylidene-2-norbornene.

In the case of polyenes other than non-conjugated alpha-omega-diolefins having 6 or more carbon atoms, these are preferably used in quantities of between 0 and 10 mol % as a second alpha-olefin comonomer.

A particular interesting embodiment of the present invention is constituted of copolymers of ethylene with propylene, 1-hexene or higher alpha-olefins.

The analysis of the distribution of the comonomer units in the copolymers of the invention has been carried out by means of ^{13}C -NMR spectroscopy. The assignments were carried out as

described by Randall in Macromol.Chem.Phys. 29, 201, 1989. The distribution of triads, in the case of ethylene/1-hexene, are calculated by the following relationship:

$$\text{HHH} = T_{\beta\beta} \quad \text{EHE} = T_{\delta\delta} \quad \text{HHE} = T_{\beta\delta} \quad \text{HEH} = S_{\beta\beta} \quad \text{HEE} = S_{\beta\delta}$$

$$\text{EEE} = 0.5(S_{\delta\delta} + 0.5S_{\beta\delta})$$

wherein EHE, HHE and HHH represent the sequence ethylene/1-hexene/ethylene, 1-hexene/1-hexene/ethylene and 1-hexene/1-hexene/1-hexene respectively in the copolymer. For the NMR nomenclature, see J.Carmen, R.A.Harrington, C.E.Wilkes, Macromolecules, 10, 537 (1977). The values are normalized. The higher the number of isolated 1-hexene units in the polymeric chain, the more the values of the ratio EHE/(EHE+HHE+HHH) become closer to the unit.

The number of 1-hexene sequences seems to be a function of the amount of 1-hexene units present in the chain.

The tables 2 and 3 refer to ethylene/1-hexene copolymers obtained with a process according to the present invention.

In particular, in table 3 there are reported the ratios EHE/(EHE+HHE+HHH) as a function of the molar percentage of 1-hexene in the chain for ethylene/1-hexene copolymers obtained with a process according to the present invention, in the presence of the above reported metallocene compounds.

In the case of ethylene/1-hexene, the reactivity ratio r_1 and the product of the reactivity ratios $r_1.r_2$ are calculated according to the following formulae as described in J.Uozomi, K.Soga, Mak. Chemie, 193, 823, (1992):

$$r_1 = 2[\text{EE}] / [\text{EH}]X$$

$$r_1.r_2 = 4[\text{EE}] \cdot [\text{HH}] / [\text{EH}]^2$$

wherein $X = [\text{E}]/[\text{H}]$ monomer molar ratio in the polymerization bath.

In the case of ethylene/propylene copolymers, the product of the reactivity ratios $r_1.r_2$, wherein r_1 is the reactivity ratio of propylene and r_2 that of ethylene, is calculated according to the following formula:

$$r_1.r_2 = 1 + f(\chi + 1) - (f + 1)(\chi + 1)^2$$

wherein

f = ratio between moles of ethylene units and moles of propylene units in the copolymer,

and

$$\chi = (\text{PPP} + \text{PPE})/\text{EPE}.$$

The molecular weight of the polymers can be varied by varying the type or the concentration of the catalyst components or using molecular weight regulators such as, for example, hydrogen.

Generally, the polymers of the present invention are endowed with a narrow molecular weight distribution. The molecular weight distribution is represented by the ratio M_w/M_n which, for the polymers of the present invention, when the metallocene used is a pure isomer, is generally lower than 4, preferably lower than 3.5 and, more preferably, lower than 3.

The molecular weight distribution can be varied by using mixtures of different metallocene compounds or by carrying out the polymerization in several stages at different polymerization temperatures and/or different concentrations of the molecular weight regulators.

The polymers of the invention are generally soluble in common solvents, such as, for instance, chloroform, hexane, heptane, toluene and xylene.

The polymers of the invention are transformable into shaped articles by conventional thermoplastic material processing such as molding, extrusion, injection etc.

The following examples are given for illustrative purposes and are not intended to limit the scope and spirit of the invention.

EXAMPLES

General procedures and characterisations:

The following abbreviations are used:

THF = tetrahydrofuran

Et_2O = ethyl ether

NaOEt = sodium ethoxide

BuOK = potassium tert-butoxide

DMSO = dimethyl sulfoxide

DMF = N,N-dimethylformamide

BuLi = butyllithium

All operations were performed under nitrogen by using conventional Schlenk-line techniques. Solvents were distilled from blue Na-benzophenone ketyl (Et_2O), CaH_2 , (CH_2Cl_2), or Al/Bu_3 (hydrocarbons), and stored under nitrogen. BuLi (Aldrich) was used as

received.

The $^1\text{H-NMR}$ analyses of the metallocenes were carried out on a Varian VXR-400 spectrometer (CD_2Cl_2 , referenced against the middle peak of the triplet of residual CHDCl_2 at 5.35 ppm). All NMR solvents were dried over P_2O_5 and distilled before use. Preparation of the samples was carried out under nitrogen using standard inert atmosphere techniques.

The $^{13}\text{C-NMR}$ and $^1\text{H-NMR}$ analyses of the polymers were carried out on a Bruker DPX 400 spectrometer operating at 400.13 MHz and 100.61 MHz respectively and were analyzed at 120°C. The powder polymer samples were dissolved in 1,1,2,2-tetrachloro-1,2-dideuteroethane ($\text{C}_2\text{D}_2\text{Cl}_4$) to give an 8% (wt./vol.) concentration. About 13000 transients were acquired with a 75° pulse and 15 seconds of delay between pulses.

Intrinsic viscosity

The measurement were carried out in a tetrahydronaphthalene (THN) solution obtained by dissolving the polymer at 135°C for 1 hour.

The melting points of the polymers (T_m) were measured by Differential Scanning Calorimetry (D.S.C.) on an instrument DSC Mettler, according to the following method. About 10 mg of sample obtained from the polymerization were cooled to -25°C and thereafter heated at 200°C with a scanning speed corresponding to 20°C minute. The sample was kept at 200°C for 5 minutes and thereafter cooled to 0°C with a scanning speed corresponding to 20°C/minute. After standing 5 minutes at 0°C, the sample was heated to 200°C at a rate of 10°C/min. In this second heating run, the peak temperature was assumed as melting temperature (T_m) and the area as global melting enthalpy (ΔH_f).

Size exclusion chromatography (SEC):

The analysis were performed by using a "WATERS 200" GPC, working at 135°C with 1,2-dichlorobenzene (stabilized with BHT, 0.1 wt.%).

PREPARATION OF THE LIGANDS

Example 1

Synthesis of 2,5-dimethyl-cyclopentadienyl-[2,1-b:3,4-b']dithiophene

Preparation of 2-Methyl-4-thiophene-aldehyd

44.26g of 2-methyl-4-bromo-thiophene (0.25mol) was dissolved in 300ml ether and treated dropwise with 164ml 1.6M BuLi (0.26mol) at -70°C. The resulting solution kept under stirring at -60- -70°C in 30min and then was treated with 27.4g dimethylformamide

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(0.37mol) in 100ml ether. The mixture was allowed to warm up to r.t., then neutralized by 10%aq. NH₄Cl, washed with 10% H₃PO₄ and finally with water up to neutral pH. The organic phase was collected, evaporated and distilled at 110°/10mmHg. Yield 22.3g (71%). The title compound was characterized by ¹H-NMR spectroscopy.

Preparation of Bis(2-methyl-4-thienyl)methane

31.3g of 2-methyl-4-bromo-thiophene (0.177mol) was dissolved in 150ml ether and treated dropwise with 113ml 1.6M BuLi (0.18mol) at -70°C. The resulting solution kept under stirring at -60 to -70°C for 30min and then was treated with 22.3g 2-methyl-4-thiophene-aldehyd (0.177mol) in 100ml ether. The mixture was allowed to warm up to r.t., then neutralized by 10%aq. NH₄Cl and washed with water. The organic phase was collected and evaporated. The suspension of 10g LiAlH₄ (0.266mol) in 100ml ether was treated dropwise with the solution of 35.5g AlCl₃ (0.266mol) in 100ml ether. The resulting mixture was treated with the solution of the compound obtained in the previous reaction in 100ml ether. The mixture refluxed for additional 1h, cooled up to r.t. and treated with 100ml ethyl acetic ester. Then the mixture was treated with 300ml H₂O and 300ml ether. Organic phase was collected, washed with water, dried with MgSO₄ and evaporated. The residue was distilled at 90-110/0.5mmHg. Yield 23.2g (63%).

The title compound was characterized by ¹H-NMR spectroscopy.

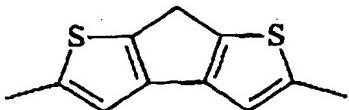
Preparation of 2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']dithiophene

1.04g of bis(5-methyl-3-thienyl)methane (5mmol) was dissolved in 30ml ether and treated at -70°C with 9ml 1.6M BuLi (15mmol) and 1.74g TMEDA (15mmol). The resulting mixture was allowed to warm to r.t., stirred in 1h, then cooled to -70°C and treated with 2.7g CuCl₂ (20mmol). The resulting mixture was allowed to warm to r.t. and treated with 30ml water. The organic phase was collected, and passed through the column with silica gel. The resulting solution was evaporated to give 0.34g of the product (34%).

The title compound was characterized by ¹H-NMR spectroscopy.

Example 2

Synthesis of 2,5-dimethyl-cyclopentadiene-[1,2-b:4,3-b']-dithiophene



(TC 5421.EP)

Preparation of 2-methyl-4-bromo-thiophene

2.5 mol AlCl₃ under stirring has been treated with 1mol of thiophenealdehyde keeping the temperature before 40C. After the liquid complex solidifies, 1.2mol Br₂ has been carefully added dropwise under stirring. After the addition the mixture solidified completely. This solid substance has been poured onto a mixture of ice (0.5kg) with hydrochloric acid (100ml, 32%), then 300ml of CH₂Cl₂ was added. The organic phase was separated and the solvent was removed. The resulting substance was dissolved in 700ml diethyleneglicole and the so-obtained solution was treated with 5.5mol 100% hydrazinehydrate. The resulting mixture was refluxed during 30min. After cooling to r.t. 2.75mol KOH has been added. After the gas evolution, the product was distilled. The fraction under 150C was collected. This fraction represented the mixture of water and the product. The organic layer was collected and distilled at 60C/10torr. Yield 52%.

The title compound was characterized by ¹H-NMR and ¹³C-NMR spectroscopy.

Preparation of 1,1-bis(3-bromo-5-methyl-thiophenyl)methane

35.4ml(0.3mol) hydrochloric acid at 0C has been treated with 36.1g(0.28mol) anhydrous ZnCl₂. After complete dissolving of ZnCl₂, the solution has been treated quickly with the solution of 70.8g(0.4mol) 3-Br-5-Me-thiophene in ether (50-100ml). The resulting mixture was treated at 0C and vigorous stirring with 23ml (0.3mol) 37% formaline within 30 min. Then the reaction mixture was stirred in additional 1h at r.t. The resulting mixture was treated with 100ml EtOH. White precipitate was isolated, washed with water, ethanol and then dried. Yield 60g(90%).

The title compound was characterized by ¹H-NMR and ¹³C-NMR spectroscopy.

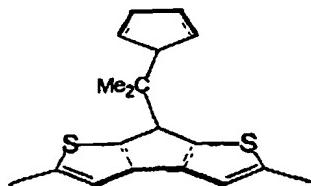
Preparation of 2,5-dimethyl-cyclopentadiene-[1,2-b:4,3-b']-dithiophene

A Solution of 0.1mol 1,1-bis(3-bromo-5-methyl-thiophenyl)methane in 200ml ether was treated with 0.23mol BuLi at -70C. After the addition is over, the mixture was stirred within additional 30min at the same temperature. White precipitate of dilithium salt forms. Then 0.265mol CuCl₂ was added quickly. The mixture was allowed to warm up to r.t. under stirring for 12 hours.

The resulting suspension was poured onto water, the organic phase was collected. The solvent was evaporated, the residue was recrystallized from ether. Yield 25%.

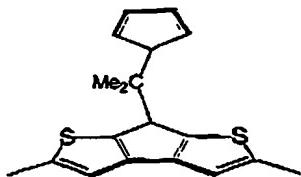
The title compound was characterized by ¹H-NMR and ¹³C-NMR spectroscopy.

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Example 3**Synthesis of 2,2-(cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)propane**

A solution of 1.03g (5mmol) of 2,5-dimethyl-cyclopentadiene-[1,2-b:4,3-b']-dithiophene in 20ml ether was treated at -70°C with 3.13ml of 1.6M BuLi (5mmol). The resulting mixture was stirred in additional 30min at 0°C, cooled again to -70°C and then was treated with 0.53g (5mmol) 6,6-dimethylfulvene in 10ml ether. The mixture was allowed to warm up to r.t. then was treated with saturated aqueous solution of NH₄Cl. The organic phase was isolated, dried and evaporated. The residue was recrystallized from hexane. Yield 1.1g (64%).

The title compound was characterized by ¹H-NMR spectroscopy.

Example 4**Preparation of 2,2-(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)propane.**

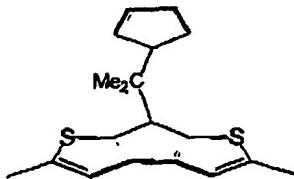
A solution of 1.03g (5mmol) of 2,5-dimethyl-cyclopentadiene-[1,2-b:4,3-b']-dithiophene in 20ml ether was treated at -70°C with 3.13ml of 1.6M BuLi (5mmol). The resulting mixture was stirred in additional 30min at 0°C, cooled again to -70°C and then was treated with 0.6g (5mmol) 3,6,6-trimethylfulvene in 10ml ether. The mixture was allowed to warm up to r.t. then was treated with saturated aqueous solution of NH₄Cl. The organic phase was isolated, dried and evaporated. The residue was recrystallized from hexane. Yield 1.0g (62%).

The title compound was characterized by ¹H-NMR spectroscopy.

(TC S421.FP)

Example 5

Synthesis of 2,2-(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)propane

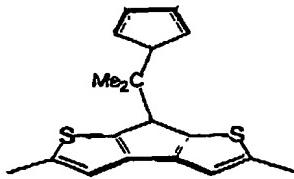


A solution of 1.03g (5mmol) of 2,5-dimethyl-cyclopentadiene-[1,2-b:4,3-b']-dithiophene in 20ml ether was treated at -70°C with 3.13ml of 1.6M BuLi (5mmol). The resulting mixture was stirred in additional 30min at 0°C, cooled again to -70°C and then was treated with 0.74g (5mmol) 3-isopropyl-6,6-dimethylfulvene in 10ml ether. The mixture was allowed to warm up to r.t. then was treated with saturated aqueous solution of NH₄Cl. The organic phase was isolated, dried and evaporated. The residue was recrystallized from hexane. Yield 0.85g (48%).

The title compound was characterized by ¹H-NMR spectroscopy.

Example 6

Synthesis of 2,2-(3-tert-butyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)propane



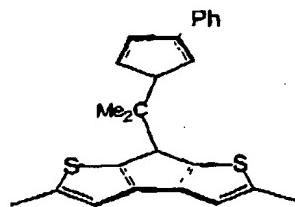
A solution of 1.03g (5mmol) of 2,5-dimethyl-cyclopentadiene-[1,2-b:4,3-b']-dithiophene in 20ml ether was treated at -70°C with 3.13ml of 1.6M BuLi (5mmol). The resulting mixture was stirred in additional 30min at 0°C, cooled again to -70°C and then was treated with 0.81g (5mmol) 3-tertbutyl-6,6-dimethylfulvene in 10ml ether. The mixture was allowed to warm up to r.t. then was treated with saturated aqueous solution of NH₄Cl. The organic phase was isolated, dried and evaporated. The residue was recrystallized from hexane. Yield 0.94g (51%).

The title compound was characterized by ¹H-NMR spectroscopy.

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Example 7

Synthesis of 2,2-(3-phenyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)propane.

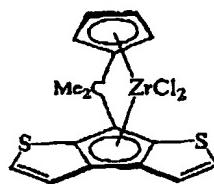


A solution of 1.03g (5mmol) of 2,5-dimethyl-cyclopentadiene-[1,2-b:4,3-b']-dithiophene in 20ml ether was treated at -70°C with 3.13ml of 1.6M BuLi (5mmol). The resulting mixture was stirred in additional 30min at 0°C, cooled again to -70°C and then was treated with 0.98g (5mmol) 2-6,6-trimethyl-4-phenyl-fulvene in 10ml ether. The mixture was allowed to warm up to r.t. then was treated with saturated aqueous solution of NH₄Cl. The organic phase was isolated, dried and evaporated. The residue was recrystallized from hexane. Yield 0.57g(29%).

The title compound was characterized by ¹H-NMR spectroscopy.

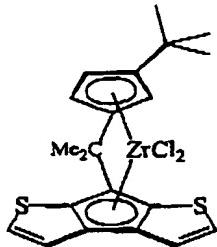
PREPARATION OF THE METALLOCENES

Preparation of isopropylidene{(cyclopentadienyl)-7-(cyclopenta[1,2-b:4,3-b']-dithiophene)}zirconium dichloride [Me₂C(Cp)(7-Th₂-Cp)ZrCl₂]



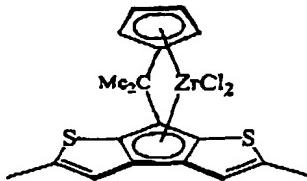
It was carried out as described in the Example 6 of WO 98/22486.

Preparation of isopropylidene(3-tertbutylcyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b'] dithiophene)zirconium dichloride [Me₂C(3-tBu-Cp)(7-Th₂-Cp)ZrCl₂]



It was carried out as described in the Example 9 of WO 98/22486

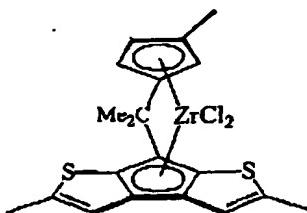
Preparation of isopropylidene(cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride [Me₂C(Cp)(7-MeTh₂-Cp)ZrCl₂]



A suspension of 1.0g (3.22mmol) of 2,2-(cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)propane in 20ml ether was treated with 4.1ml (6.5mmol) 1.6M BuLi at -70°C. The mixture was allowed to warm up to 0°C and then was treated with 0.75g (3.2mmol) ZrCl₄. The reaction mixture was stirred at reflux within 3h, then the yellow precipitate was filtered, washed twice with ether, dried and then recrystallized from CH₂Cl₂. Yield 1.37g (90%).

The title compound was characterized by ¹H-NMR and ¹³C-NMR spectroscopy.

Preparation of isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride [Me₂C(3-Me-Cp)(7-MeTh₂-Cp)ZrCl₂]



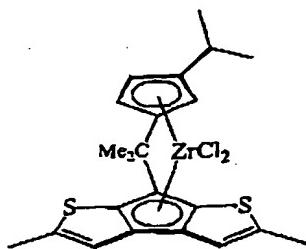
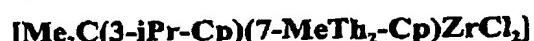
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Suspension of 0.6g (1.85mmol) of 2,2-(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)propane in 20ml ether was treated with 2.3ml (3.7mmol) 1.6M BuLi at -70°C. The mixture was allowed to warm up to 0°C and then was treated with 0.43g (1.85mmol) ZrCl₄. The reaction mixture was stirred at reflux within 3h, then the yellow precipitate was filtered, washed twice with ether, dried and then recrystallized from CH₂Cl₂. Yield 0.72g (80%).

The title compound was characterized by ¹H-NMR and ¹³C-NMR spectroscopy.

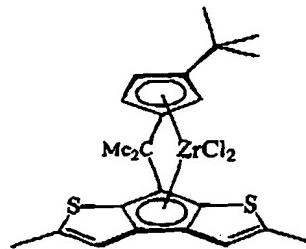
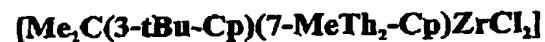
Preparation of isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride



A suspension of 1.06g (3.0mmol) of 2,2-(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)propane in 20ml ether was treated with 3.75ml (6.0mmol) 1.6M BuLi at -70°C. The mixture was allowed to warm up to 0°C and then was treated with 0.7g (3.0mmol) ZrCl₄. The reaction mixture was stirred at reflux within 3h, then the yellow precipitate was filtered, washed twice with ether, dried and then recrystallized from CH₂Cl₂. Yield 1.24g (80%).

The title compound was characterized by ¹H-NMR and ¹³C-NMR spectroscopy.

Preparation of isopropylidene(3-tert-butyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride



A suspension of 1.11g (3.0mmol) of 2,2-(3-tert-butyl-cyclopentadienyl)-7-(2,5-dimethyl-

cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)propane in 20ml ether was treated with 3.75ml (6.0mmol) 1.6M BuLi at -70°C. The mixture was allowed to warm up to 0°C and then was treated with 0.7g (3.0mmol) ZrCl₄. The reaction mixture was stirred at reflux within 3h, then the yellow precipitate was filtered, washed twice with ether, dried and then recrystallized from CH₂Cl₂. Yield 1.27g (80%).

The title compound was characterized by ¹H-NMR and ¹³C-NMR spectroscopy.

POLYMERIZATION

Methylalumoxane (MAO)

A commercial (Witco) 10 % toluene solution was dried in vacuum until a solid, glassy material was obtained which was finely crushed and further treated in vacuum until all volatiles were removed (4-6 hours, 0.1 mmHg, 50°C) to leave a white, free-flowing powder.

Tris(2,4,4-trimethyl-pentyl)aluminum (TIOA)

A commercial (Witco) sample was used diluted to a 1 M solution in the indicated solvent.

Preparation of TIOAO

5 ml of toluene and 3.5 mmol (3.5 ml) of TIOA solution (1 M in hexane) are introduced in a Schlenk tube. Then 1.75 mmol (31.5 µl) of H₂O are added, and the resultant solution is stirred for 10 minutes at room temperature.

Polymerization Example 1 to 6

Ethylene polymerization in a glass autoclave

Ethylene polymerization under standard conditions was performed in a 200 ml glass autoclave, provided with magnetic stirrer, temperature indicator and feeding line for the ethylene. It was purified and fluxed with ethylene at 35°C. 90 ml of hexane were introduced at room temperature. The catalytic system was prepared separately in 10 ml of hexane by consecutively introducing the Aluminum alkyl, MAO or TIOA/water (Al/H₂O=2.1), and after 5 minutes of stirring, the metallocene solved in toluene (the lowest amount as possible). After 5 minutes of stirring the solution was introduced into the autoclave under ethylene flow. The reactor was closed, the temperature risen to 80°C and pressurized with ethylene to 4.6 bar. The total pressure was kept constant by feeding ethylene. After the time indicated in Table 1, the polymerization was stopped by cooling, degassing the reactor and introducing 1 ml of methanole. The achieved polymer was washed with acidic methanol,

than with methanol and dried in an oven at 60°C under vacuum.

The polymerization conditions and the characterization data of the polymer obtained are reported in Table 1.

Polymerization Example 7

The general procedure described in Ex. 1-6 was followed, except that the metallocene indicated in Table 1 were used and the polymerization was carried out in heptane (150 ml) instead of hexane and by using a 260 ml glass autoclave.

The polymerization conditions and the data relating to the obtained polymer are indicated in Table 1.

Polymerization Examples 8 and 9 (Comparison)

The general procedure described in Ex. 1-6 was followed, except that the metallocenes indicated in Table 1 were used.

The polymerization conditions and the data relating to the obtained polymer are indicated in Table 1.

Polymerization Examples 10 to 12

Ethylene polymerization in a steel autoclave

A 1 L steel autoclave, provided with magnetic stirrer, temperature indicator and feeding line for the monomers was purified and fluxed with ethylene at 80°C. At room temperature it was introduced 500 ml of hexane and 1 mmol of TIBAL as a scavenger. The catalytic system was prepared separately in a 10 ml schlenk tube by consecutively introducing MAO (10 wt% vol in toluene) and the metallocene solved in toluene (the lowest amount as possible). After 10 minutes of stirring the solution was injected into the autoclave through a vial by an ethylene overpressure, the temperature risen to 80°C and pressurized with ethylene to a final pressure of 10 bar. The total pressure was kept constant by feeding ethylene. After 1 h the polymerization was stopped by cooling and introducing 1 bar of carbon monoxide. Then the reactor was degassed and the polymer was recovered by filtration and dried in an oven at 60°C under vacuum.

The polymerization conditions and the data relating to the obtained polymer are indicated in Table 1.

Polymerization Examples 13 t 16

Ethylene/1-hexene copolymerization

In a 260 ml glass autoclave, provided with magnetic stirrer, temperature indicator and feeding line for ethylene was purified and fluxed with ethylene at 35°C. At room temperature it was introduced heptane to reach the final volume and 1-hexene in the amounts as indicated in Table 2. The catalytic system was prepared separately in 10 ml of heptane by consecutively introducing the MAO and the metallocene solved in 3 ml of toluene. After 5 minutes of stirring the solution was introduced into the autoclave under ethylene flow. The reactor was closed, the temperature risen to 70°C and pressurized to 4.5 bar. The total pressure was kept constant by feeding ethylene. After 15 minutes the polymerization was stopped by cooling, degassing the reactor and introducing 1 ml of methanol. The achieved polymer was washed with acidic methanol, then with methanol and dried in an oven at 60°C under vacuum.

The polymerization conditions and the data relating to the obtained polymer are indicated in Tables 2 and 3.

Polymerization Examples 17 and 18 (Comparison)

The general procedure described in Ex. 13-16 was followed, except that the polymerization was carried out in a 200 ml glass autoclave and by using 100 ml as total liquid volume.

The polymerization conditions and the data relating to the obtained polymer are indicated in Tables 2 and 3.

Polymerization Examples 19 to 22 and 23 (Comparison)

Ethylene/propylene copolymerization

Polymerizations were performed at 50°C, in a 250 mL glass reactor, equipped with a mechanical stirrer, a thermometer and a pipe for monomers feeding. 100 mL of toluene and the TIOAO solution, fresh prepared as described above (3.45 mmol of Aluminum) was introduced in the nitrogen-purged reactor, kept in a thermostatic bath. At the polymerization temperature, a ethene/propylene gaseous mixture (60 wt% of ethene) was fed and continuously discharged with a flow of 1.5 L/min and a pressure of 1.1 atm. After 2 minutes, 3.45 µmol of catalyst, dissolved in 5 mL of toluene in the presence of 34 µmoles of TIOA, were added to start the polymerization. During the polymerization, the temperature was kept within ± 0.2°C. The polymerization was stopped after 15 min by

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adding 1 mL of methanol and the copolymer was recovered by precipitation in methanol/HCl and filtration and finally dried at 50°C under reduced pressure.

The polymerization conditions and the data relating to the obtained polymer are indicated in Table 4.

Polymerization Examples 24 to 27

Ethylene/propylene/ENB terpolymerization

Polymerizations were performed at 50°C, in a 250 mL glass reactor, equipped with a mechanical stirrer, a thermometer and a pipe for monomers feeding. 100 mL of toluene, 2 mL of ENB and 1.2 mL of MAO solution (2.0 mmol of Aluminum) were introduced in the nitrogen-purged reactor, kept in a thermostatic bath. At the polymerization temperature, a ethene/propylene gaseous mixture (60 wt% of ethene) was fed and continuously discharged with a flow of 1.5 L/min and a pressure of 1.1 bar. After 2 minutes 2.0 μ mol of catalyst, dissolved in 5 mL of toluene in the presence of 20 μ moles of MAO, were added to start the polymerization. During the polymerization, the temperature was kept within $\pm 0.2^\circ\text{C}$. The polymerization was stopped after 15 min by adding 1 mL of methanol and the copolymer was recovered by precipitation in methanol/HCl and filtration and finally dried at 50°C under reduced pressure

The polymerization conditions and the data relating to the obtained polymer are indicated in Table 5.

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Table 1 (ethylene homopolymerization)

Example	Zirconocene dichloride	AlR ₃	Type	(mg)	(mmol)	Al/Zr	1-hexane	Time	yield	activity	I.V.
				(mg)	(mol)	(mol)	(ml)	(min)	(g)	(Kg/gZr.h)	(dL/g)
1	CMe ₂ (3-iBu-Cp)(7-Th ₂ Cp)	0.4	MAO	2.3	3000	100	5	1.5	256.9	3.97	-
2	CMe ₂ (3-iBu-Cp)(7-Th ₂ Cp)	0.3	TiOA-H ₂ O	1.7	3000	100	20	0.09	5.1	-	-
3	CMe ₂ (Cp)(7-MeTh ₂ Cp)	0.1	MAO	0.22	1050	100	10	1.0	306.1	3.4	-
4	CMe ₂ (3-Me-Cp)(7-MeTh ₂ Cp)	0.1	MAO	0.22	1060	100	8	1.65	663.0	4.0	-
5	CMe ₂ (3-iBu-Cp)(7-MeTh ₂ Cp)	0.08	MAO	0.16	1000	100	10	2.13	929.6	>4.3	-
6	CMe ₂ (3-iBu-Cp)(7-MeTh ₂ Cp)	0.11	MAO	0.21	1060	100	2	1.0	1496.4	-	-
7	CMe ₂ (3-iPr-Cp)(7-MeTh ₂ Cp)	0.11	MAO	0.23	1080	150*	15	5.8	1196.4	4.5	-
8 (comp.)	CMe ₂ (Cp)(7-Th ₂ Cp)	0.5	MAO	1.2	1060	100	10	1.7	97.7	2.6	-
9 (comp.)	CMe ₂ (Cp)(7-Th ₂ Cp)	0.5	TiOA-H ₂ O	1.16	1030	100	30	0.05	1.0	-	-
10	CMe ₂ (Cp)(7-MeTh ₂ Cp)	0.5	MAO	0.21	200	500	60	15.3	159.2	2.1	-
11	CMe ₂ (3-Me-Cp)(7-MeTh ₂ Cp)	0.4	MAO	0.16	195	500	60	21.1	282.6	2.3	-
12	CMe ₂ (3-iBu-Cp)(7-MeTh ₂ Cp)	0.3	MAO	0.11	185	500	60	30.1	583.3	5.1	-

*1-heptane

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Table 2 (ethylene/1-hexene copolymerization)

Example	Zirconocene dichloride Type	AlR ₃ (mg)	Type (mmol)	Al/Zr (mol)	1-hexene (ml)	Time (min)	yield (g)	activity (Kg/gZr.h)	I.V. (dL/g)
13	CMe ₂ (3-Me-Cp)(7-MeTh ₂ Cp)	0.10	MAO	0.23	1000	10	15	1.89	404.9
14	CMe ₂ (3-iBu-Cp)(7-MeTh ₂ Cp)	0.11	MAO	0.22	1060	10	15	1.59	336.3
15	CMe ₂ (3-iPr-Cp)(7-MeTh ₂ Cp)	0.11	MAO	0.23	1080	5	15	3.48	713.8
16	CMe ₂ (3-iPr-Cp)(7-MeTh ₂ Cp)	0.11	MAO	0.23	1080	10	20	0.67	103.0
17	CMe ₂ (Cp)(7-MeTh ₂ Cp)	0.10	MAO	0.23	1070	2	10	2.36	736.9
18 (comp)	CMe ₂ (Cp)(7-Th ₂ Cp)	0.50	MAO	1.20	1170	10	15	3.86	1165.5
								0.71	

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Table 3 (ethylene/1-hexene copolymerization)

Example	Zirconocene dichloride	1-hexene (mol%)	Tm (°C)	ΔH (J/g)	N.M.R			r_1	r_1, r_2
					HHH	HHE	EHE/ (EHE+HHE+HHH) (%mol)		
13	CMe ₂ (3-Me-Cp)(7-MeTh ₂ Cp)	11.6	72.5	40.2	9.94	0	1.71	0.85	9.58 0.531
14	CMe ₂ (3-tBu-Cp)(7-MeTh ₂ Cp)	11.5	74.5	33.5	8.89	0.38	2.20	0.77	10.48 1.086
15	CMe ₂ (3-Pr-Cp)(7-MeTh ₂ Cp)	-	100.3	90.5	-	-	-	-	-
16	CMe ₂ (3-Pr-Cp)(7-MeTh ₂ Cp)	6.7	93.5	60.9	5.99	0	0.74	0.89	17.5 0.686
17#	CMe ₂ (Cp)(7-MeTh ₂ Cp)	4.3	106.0	108	4.16	0	0.14	0.96	7.35 0.383
18 (comp.)#	CMe ₂ (Cp)(7-Th ₂ Cp)	17.9	45*	8*	14.93	0.27	2.71	0.83	7.05 0.410

* data from the first heating

Table 4 (ethylene/propylene copolymerization)

Example	Zirconocene dichloride Type	Al/Zr (mg)	Time (min)	Yield (g)	Activity (Kg(gZr.h))	C ₂ (mol%)	I.V. (dL/g)	r ₁ r ₂
19	CMe ₂ (3-Me-Cp)(7-MeTh ₂ Cp)	1.7	1000	15	4.97	63.2	78.8	0.68
20	CMe ₂ (3-iBu-Cp)(7-MeTh ₂ Cp)	1.8	1000	15	5.9	74.8	72.2	1.17
21	CMe ₂ (3-iPr-Cp)(7-MeTh ₂ Cp)	0.9	2000	15	3.48	87.2	75.7	0.69
22	CMe ₂ (Cp)(7-MeTh ₂ Cp)	1.6	1000	15	2.86	36.4	79.1	0.60
23 (comp)	CMe ₂ (Cp)(7-Th ₂ Cp)	1.4	1000	15	1.35	19.5	72.3	0.51

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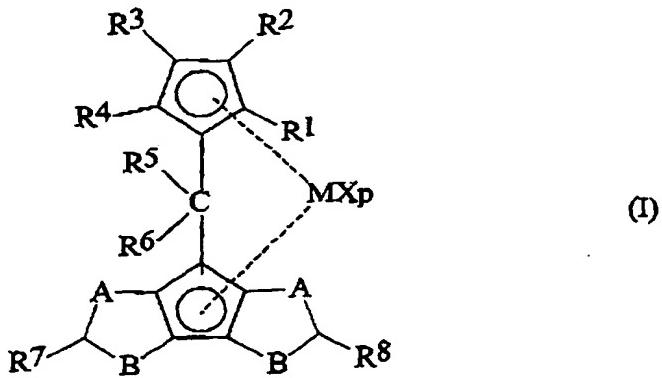
Table 5 (ethylene/propylene/ENB polymerization)

Example	Zirconocene dichloride Type	Al/Zr (mg)	Time (min)	yield (g)	Activity (Kg/gZr.h)	I.V. (dL/g)	C ₂ (mol%)	ENB (mol%)
24	CMe ₂ (3-Me-Cp)(7-MeTh ₂ Cp)	1.3	1000	15	3.45	57.6	0.37	72.5
25	CMe ₂ (3-iBu-Cp)(7-MeTh ₂ Cp)	1.4	1000	15	1.98	33.2	n.d.	77.8
26	CMe ₂ (3-iPr-Cp)(7-MeTh ₂ Cp)*	1.3	2000	15	9.85	166.0	0.42	55.2
27	CMe ₂ (Cp)(7-MeTh ₂ Cp)	1.2	1000	15	1.35	22.8	0.35	72.3
								15.5

n.d. not determined

CLAIMS

1. A process for the preparation of ethylene polymers, comprising the polymerization reaction of ethylene and optionally at least one alpha-olefin, in the presence of a catalyst obtainable by contacting:
- (A) a metallocene compound of the formula (I) :



wherein

A and B are selected from S, O and CR⁹, R⁹ being selected from hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, C₇-C₂₀-arylalkyl radical, optionally containing a heteroatom, either A or B being different from CR⁹, and wherein the rings containing A and B have a double bond in the allowed position;

R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, and R⁹, same or different, are selected from hydrogen, a C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl, C₂-C₂₀-alkenyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl, C₇-C₂₀-arylalkyl radical, optionally containing a heteroatom, and two adjacent R¹ and R² and/or R³ and R⁴ and/or R⁵ and R⁶ can form a ring comprising 4 to 8 atoms, which can bear substituents;

with the proviso that at least one of R¹, R², R³, R⁴, R⁷ and R⁸ is different from hydrogen;

M is an atom of a transition metal selected from those belonging to group 3, 4, 5, 6 or to the lanthanide or actinide groups in the Periodic Table of the Elements (new IUPAC version),

X, same or different, is a halogen atom, a R¹⁰, OR¹⁰, OSO₂CF₃, OCOR¹⁰, SR¹⁰,

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NR^{10}_2 or PR^{10}_2 group, wherein the substituents R^{10} are selected from hydrogen, a $\text{C}_1\text{-C}_{20}$ -alkyl, $\text{C}_3\text{-C}_{20}$ -cycloalkyl, $\text{C}_2\text{-C}_{20}$ -alkenyl, $\text{C}_6\text{-C}_{20}$ -aryl, $\text{C}_7\text{-C}_{20}$ -alkylaryl, $\text{C}_7\text{-C}_{20}$ -arylalkyl radical, optionally containing a heteroatom;
 p is an integer of from 0 to 3, being equal to the oxidation state of the metal M minus 2

and

- (B) an alumoxane and/or a compound capable of forming an alkyl metallocene cation.
- 2. The process according to claim 1, wherein in the metallocene compound of formula (I) the transition metal M is selected from titanium, zirconium and hafnium.
- 3. The process according to any of claims 1 to 2, wherein in the metallocene compound of formula (I) the X substituents are chlorine atoms or methyl groups.
- 4. The process according to any of claims 1 to 3, wherein in the metallocene compound of formula (I) A and B are selected from sulfur and a CH group, either A or B being different from CH, R^5 and R^6 are $\text{C}_1\text{-C}_{20}$ -alkyl groups, and R^7 is equal to R^8 .
- 5. The process according to claim 4, wherein R^1 , R^3 and R^4 are hydrogen, R^5 and R^6 are methyl, R^2 are hydrogen or $\text{C}_1\text{-C}_{20}$ -alkyl groups and R^7 and R^8 are hydrogen or methyl groups.
- 6. The process according to any of claims 1 to 5, wherein the metallocene compound of formula (I) is
 isopropylidene(3-tert-butyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride,
 isopropylidene(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride,
 isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride,
 isopropylidene(cyclopentadienyl)-7-(2,5-dimethyl-cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride and
 isopropylidene(3-tert-butyl-cyclopentadienyl)-7-(cyclopentadienyl-[1,2-b:4,3-b']-dithiophene)zirconium dichloride.
- 7. The process according to claim 1, wherein said alumoxane is obtained by contacting

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water with an organo-aluminium compound of formula AlR^{11} , or $Al_2R^{11}_6$, wherein the R^{11} substituents are defined as R^1 .

8. The process according to claim 7, wherein the molar ratio between the aluminium and water is in the range of 1:1 and 100:1.
9. The process according to any of claim 1, wherein said alumoxane is MAO, TIBAO and TIOAO, and said organo-aluminium compound is TIOA, TMA and/or TIBA.
10. The process according to claim 1, wherein the compound capable of forming a metallocene alkyl cation is a compound of formula Y^+Z^- , wherein Y^+ is a Bronsted acid, able to give a proton and to react irreversibly with a substituent X of the metallocene of formula (I) and Z^- is a compatible anion, which does not coordinate, which is able to stabilize the active catalytic species originating from the reaction of the two compounds, and which is sufficiently liable to be able to be removed from an olefinic substrate.
11. The process according to claim 10, wherein the anion Z^- comprises one or more boron atoms.
12. The process according to any of claims 1 to 11, wherein said process is carried out at a temperature comprised between -100 and +200°C and at a pressure comprised between 0,5 and 100 bar.
13. The process according to any of claims 1 to 12, wherein the molar ratio between the aluminium and the metal of the metallocene compound is comprised between 10:1 and 20000:1.
14. The process according to any of claims 1 to 13, wherein said process is used for the preparation of homo- and copolymers of ethylene.
15. The process according to any of claims 1 to 14, wherein the process is carried out in the presence of an alpha-olefin selected from propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene and 1-dodecene.
16. The process according to claim 15, wherein said alpha-olefin is 1-hexene or propylene.
17. The process according to any of claims 15 to 16, wherein the molar content of alpha-olefin derived units is comprised between 0% and 60%.
18. The process according to any of claims 1 to 17, wherein the process is carried out in

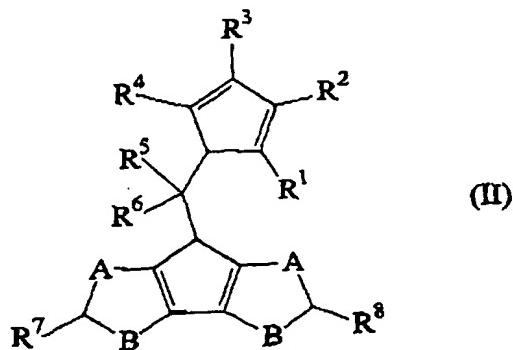
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the presence of a cyclic comonomer.

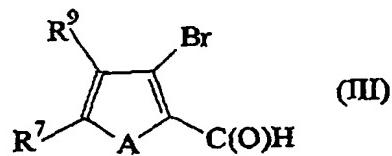
19. The process according to claim 18, wherein the cyclic comonomer is 5-ethyliden-2-norbornene.
20. The process according to any of claims 18 to 19, wherein the molar content of the cyclic comonomer is comprised between 0% and 30% by mol.
21. A process for the preparation of a ligand of formula (II):



and/or its double bond isomers,

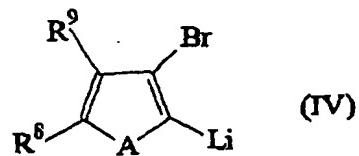
wherein A, B, R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ are defined as above, comprising the following steps:

- a) treating a compound of formula (III):



wherein A is sulfur or oxygen,

with a compound of formula (IV):



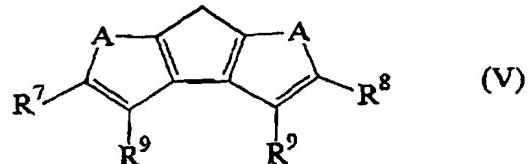
wherein A is sulfur or oxygen,

- b) contacting the thus obtained product with a reducing agent in a molar ratio between said reducing agent and the product obtained under a) of at least 1;
- c) contacting the product obtained under b) with a compound selected from an

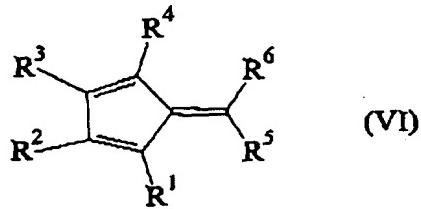
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organic lithium compound, sodium and potassium in a molar ratio between said compound and the product obtained in step b) of equal to or greater than 2;

- d) treating the thus obtained product with an agent selected from the group consisting of copper chloride, iodine and Mg/Pd, in order to obtain a compound of general formula (V):

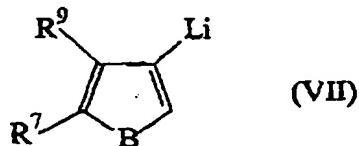


- e) treating the compound of formula (V) with at least one equivalent of a base;
 f) contacting the thus obtained corresponding anionic compound of formula (V) with a compound of formula (VI):



wherein R¹, R², R³, R⁴, R⁵ and R⁶ are defined as described in claim 1, and

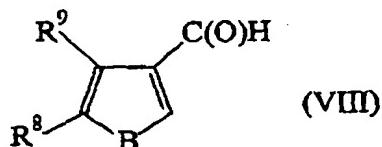
- g) treating the thus obtained product with a protonating agent.
 22. A process for the preparation of a ligand of formula (II) as defined in claim 21, comprising the following steps:
 a) contacting a compound of formula (VII):



wherein B is sulfur or oxygen,

with a compound of formula (VIII):

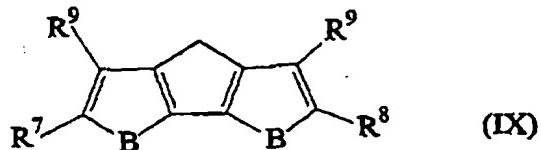
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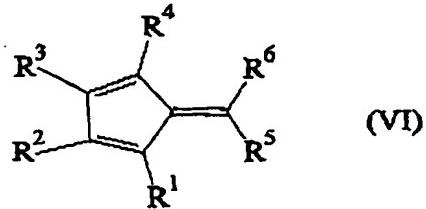
wherein B is sulfur or oxygen,

and subsequently treating with a neutralization agent;

- b) treating the thus obtained product with a reducing agent in a molar ratio between said reducing agent and the compound obtained under a) of at least 1;
- c) contacting the thus obtained product with a mixture of an organic lithium compound and tetramethylethylenediamine (TMEDA) in a molar ratio between said mixture and the product obtained under b) of at least 2,
- d) contacting the thus obtained product with an agent selected from the group consisting of copper chloride, iodine and Mg/Pd., in order to obtain a compound of formula (IX):



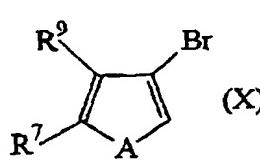
- e) treating the compound of formula (IX) with at least one equivalent of a base;
- f) contacting the thus obtained corresponding anionic compound of formula (IX) with a compound of formula (VI):



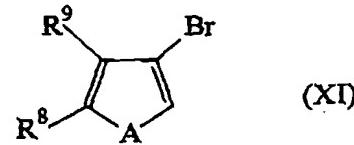
wherein R¹, R², R³, R⁴, R⁵ and R⁶ are defined as described in claim 21, and

- g) treating the thus obtained product with a protonating agent.
23. A process for the preparation of a ligand of formula (II) as defined in claim 1, comprising the following steps:
- a) contacting an equimolar mixture of compounds of formulae (X) and (XI):

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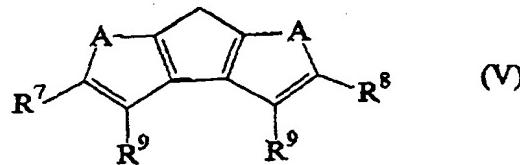
and



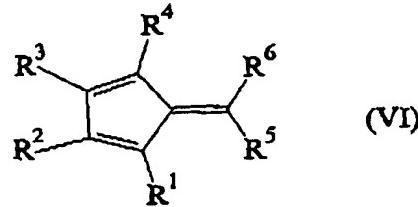
wherein A are sulfur or oxygen,

with a Lewis acid or a mixture of a Lewis acid and a protonic acid;

- b) treating the thus obtained product with CH₂O in a molar ratio between said mixture and CH₂O of a range between 10:1 and 1:10;
- c) contacting the thus obtained product with a compound selected from an organic lithium compound, sodium and potassium;
- d) contacting the thus obtained product with an agent selected from the group consisting of copper chloride, iodine and Mg/Pd., in order to obtain a compound of general formula (V)



- e) treating the compound of formula (V) with at least one equivalent of a base;
- f) contacting the thus obtained corresponding anionic compound of formula (V) with a compound of formula (VI):

wherein R¹, R², R³, R⁴, R⁵ and R⁶ are defined as described in claim 1, and

- g) treating the thus obtained product with a protonating agent.
- 24. The process according to any of claims 21 to 23, wherein the agent is copper chloride.
- 25. Process according to any of claims 21 to 24, wherein the base is selected from hydroxides and hydrides of alkali- and earth-alkali metals, metallic sodium and potassium and organometallic lithium salts.
- 26. The process according to claim 25, wherein the base is methylolithium or n-

butyllithium.

27. The process according to any of claims 21 to 26, wherein the Lewis acid is selected from zinc dichloride, cadmium dichloride, mercurium dichloride, tin tetrachloride, trifluoroborane, zirconium tetrachloride, titanium tetrachloride.

28. The process according to claim 27, wherein the Lewis acid is zinc dichloride.

29. The process according to any of claims 21 to 28, wherein the protonic acid is selected from sulphuric acid, phosphoric acid, nitric acid and hydrochloric acid.

30. The process according to claim 29, wherein hydrochloric acid is used.

31. The process according to claims 21 to 23, wherein the protonating agent used in above step o) is a quaternary ammonium salts.

32. The process according to claim 31, wherein the protonating agent is ammonium chloride.

33. The process according to any of claims 21 to 23, wherein the reducing agent is a mixture of $\text{AlCl}_3/\text{LiAlH}_4$.

34. A process for the preparation of a metallocene compound of the formula (I): comprising the following steps:
a) contacting a compound of formula (II) as defined in claim 21 with a base, wherein the molar ratio between said base and the compound of formula (II) is at least 2;
b) contacting with a compound of formula (XII) MX_p , M and X being defined as in claim 1 and p is an integer being equal to the oxidation state of the metal M.

35. The process according to claim 34, wherein the base is butyllithium.

36. The process according to claim 34, wherein MX_p is ZrCl_4 , TiCl_4 , HfCl_4 and their $\text{C}_1\text{-C}_6$ -alkyl analogues.

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ABSTRACT:

Ethylene based polymers having high molecular weights can be obtained in high yields at temperatures of industrial interest, by carrying out the polymerization reaction in the presence of catalysts comprising single carbon bridged metallocenes, which has a particular ligand system containing a heteroatom.

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